

Electronic Transition Moment Integrals for First Ionization of CO and the A–X Transition in CO⁺. Some Limitations on the use of the *r*-Centroid Approximation *

Paul H. Krupenie

Institute for Basic Standards, National Bureau of Standards, Washington, D.C. 20234

and

William Benesch

Institute for Molecular Physics, University of Maryland, College Park, Maryland 20742

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Integrals necessary for the determination of transition moment matrix elements from experimental data have been evaluated numerically by use of vibrational wave functions derived from RKR potentials. A power series expansion for the electronic transition moment has been assumed. The significant quantities which can be related to an arbitrary center of expansion are vibrational overlap integrals and quantities of the form $\int \psi_e r^n \psi_v dr$. Experimental band intensities and relative populations for vibrational levels of the initial electronic state are needed to determine the expansion coefficients. Transition moment integrals have been calculated for first ionization from the ground electronic state of CO and for the $A^2\Pi_i - X^2\Sigma^+$ transition of CO⁺. Comparison of these integrals with previous calculations based on Morse functions has shown them to be rather sensitive to the wave-functions [potentials] used. Characteristics generally attributed to the *r*-centroid and related integrals are examined, and some limitations on the use of the *r*-centroid approximation are discussed, following a review of assumptions made in the use of that approximation.

Key Words: Electronic transition moment integrals; Franck-Condon factors; Franck-Condon principle; transition probabilities; CO; CO⁺.

1. Introduction

Quantitative determination of transition probabilities for diatomic molecules is generally based on the "dipole approximation", the bases and limitations of which have been stated by Bethe and Salpeter [1]. The length form for the transition moment matrix element is commonly used for simplicity. Herzberg [2] has given the basis for the approximate separation of nuclear and electronic multipole moments so that only the electronic contribution need be considered. The Born-Oppenheimer approximation is assumed valid, i.e.,

$$\psi_{\text{total}}(x, r) \approx \psi_e(x, r) \psi_v(r) \quad (1)$$

where *r* is the internuclear distance and *x* refers to the electronic coordinates. Vibration-rotation interaction and isotope effects are not considered here.

Intensities of electronic-vibrational bands or radiative lifetimes of vibrational energy levels are most often used to provide the measures of transition probabilities. This discussion emphasizes the use of intensities.

The integrated intensity of an electronic-vibrational band (electric dipole transition) is given by [2]

$$I_{v'v''} = N_{v'} A_{v'v''} h c \sigma_{v'v''} = \text{const. } N_{v'} \sigma_{v'v''}^A |R_{v'v''}|^2 \quad (2)$$

for emission, and by

$$I_{v'v''} = \text{const. } N_{v''} \sigma_{v'v''} |R_{v'v''}|^2 \quad (3)$$

for absorption. $N_{v'}$ and $N_{v''}$ are the populations of levels v' and v'' , $A_{v'v''}$ is the transition probability for spontaneous emission, $\sigma_{v'v''}$ is the wave number of the

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transition, and $R_{v'v''}$ is the multipole moment matrix element whose square is the band strength, $S_{v'v''}$. The transition probability is proportional to the square of the matrix element [2] which is given by

$$R_{v'v''} = \int \psi_{v'}(r) R_e(r) \psi_{v''}(r) dr \quad (4)$$

where the electronic transition moment is given by

$$R_e(r) = \int \psi_{e'}(x, r) M(x) \psi_{e''}(x, r) dx. \quad (5)$$

$\psi_{v'}$ and $\psi_{v''}$ are the vibrational wave functions for levels v' and v'' , $\psi_{e'}$ and $\psi_{e''}$ are the corresponding electronic wave functions, and $M(x)$ is the electric multipole moment, a function only of electronic coordinates (e.g., electronic dipole moment is $e\Sigma x_i$).

For an electric quadrupole or magnetic multipole transition, the more complicated expressions analogous to (5) still reduce to some function of internuclear distance, $R_e(r)$.

There exists ambiguity about some quantities which appear in (2) and (3). A characteristic wave number for the band is not clearly defined. If absolute intensities are considered then the constants include statistical weights of the upper and lower electronic states. Transition moment and band strength have been defined in the literature in several different ways. A critical discussion of these and related topics has recently been given by Tatum [3].

$R_e(r)$ usually cannot be calculated from first principles because of insufficient knowledge about electronic wave functions, so we assume that R_e can be approximated by

$$R_e(r) = R_0 + R_1(r - r_0) + R_2(r - r_0)^2 + \dots \quad (6)$$

where r_0 is some meaningful center of expansion for the electronic transition. A possible choice for r_0 is $(r'_e + r''_e)/2$ which will generally lie within a region where both $\psi_{v'}$ and $\psi_{v''}$ are nonvanishing; however, this choice is arbitrary. An r_0 "characteristic" of the 0-0 transition has been suggested in the literature, but this is not always a useful choice when $|r'_e - r''_e|$ is large, since the 0-0 transition may not be easily observable.

It is tempting to consider (6) a Taylor series and to relate the expansion coefficients, R_i , to derivatives of $R_e(r)$; however, the use of generally imprecise data on intensities and vibrational populations, together with the inclusion of only a few terms in the expansion, makes this procedure uncertain. The transition moment can be simply approximated as

$$R_e(r) = R_0 + R_1 r + R_2 r^2 + \dots \quad (6a)$$

and the empirical coefficients R_i obtained by using the observed values of I , σ , and N in (2) or (3), and employing the method of least squares.

Substitution of (6a) into (4) gives the matrix element

$$R_{v'v''} = R_0(v', v'') + R_1(v', rv'') + R_2(v', r^2v'') + \dots \quad (7)$$

the square of which is the band strength. In (7) integrals of the form $\int \psi_{v'} r^n \psi_{v''} dr$ are indicated by $(v', r^n v'')$. In the r -centroid approximation [4], the square of (7) is approximated as

$$S_{v'v''} = - |R_{v'v''}|^2 \approx R_e^2(\bar{r}_{v'v''}) q_{v'v''}. \quad (8)$$

The band strength is written as the Franck-Condon factor [square of the vibration overlap integral] times the square of the transition moment as a function of r -centroid which is

$$\bar{r}_{v'v''} = \frac{(v', rv'')}{(v', v'')}. \quad (9)$$

Separability of the total wave functions in the Born-Oppenheimer approximation does not necessarily imply the factorability of the band strength into an electronic part times a vibrational part. That factorization is based on an assumed form [r -dependence] for the intermediate parameter, the transition moment.

For constant $R_e(r)$, $S_{v'v''}$ includes only a single term, $R_0^2 q_{v'v''}$, and the Franck-Condon factor contains all the relative band-to-band variation. For linear $R_e(r)$, (7) becomes

$$R_{v'v''} = R_0(v', v'') + R_1(v', rv'') \quad (7a)$$

or

$$R_{v'v''} = (v', v'') (R_0 + R_1 \bar{r}_{v'v''}) \quad (7b)$$

and $S_{v'v''}$ has the form of (8) [5, 4]. In the r -centroid approximation the assumption is made that the band strength is also factorable as in (8) for [slowly varying] nonlinear $R_e(r)$. This is based on the assumed near equality of ratios [4]

$$\bar{r}_{v'v''} = \frac{(v', rv'')}{(v', v'')} \approx \frac{(v', r^2v'')}{(v', rv'')} \approx \frac{(v', r^n v'')}{(v', r^{n-1}v'')} \quad (10)$$

up to perhaps $n \approx 10$. A consequence of this assumption is [4] that, for any reasonable function, $f(r)$,

$$(v', f(r)v'') = f(\bar{r}_{v'v''}) (v', v'') \quad (11)$$

which, in particular, always implies (8). Our numerical calculations on the ratios of (10) for the ionization transition $(X^2\Sigma^+) \text{ CO}^+ - (X^1\Sigma^+) \text{ CO}$ and the A-X transition in CO^+ suggest that for nonlinear R_e , the band strength may not always be factored according to (8) [6].

An implicit assumption made in this type of calculation is that R_e must be a slowly varying function of r [2]. How slowly varying this should be is not clear. Nevertheless, in several cases [7], significant variation has been deduced from use of experimental intensities and (2) and (8). It is, of course, possible for an appreciable apparent variation in R_e over a small range of r to arise from inaccurate intensity measurements, inaccurate values of $q_{v'v''}$, or the possibly invalid approximation (8).

Tyte [8] has cautioned against the casual use of experimental intensities in determining the form of the transition moment, for the relative intensity distribution may depend on experimental conditions. There are also built-in complications in the use of intensities because of blended rotational structure and partial overlap of bands.

The use of radiative lifetimes for determining $R_e(r)$ is even more complicated than use of intensities as can be seen from the following equation

$$\tau_{v'} = \frac{1}{\sum_{v''} A_{v'v''}} = \frac{1}{\text{const.} \sum_{v''} \sigma_{v'v''}^3 |R_{v'v''}|^2} \quad (12)$$

2. Transition Moment Integrals for $X^2\Sigma^+(\text{CO}^+) - X^1\Sigma^+(\text{CO})$ and $A^2\Pi_i(\text{CO}^+) - X^2\Sigma^+(\text{CO}^+)$

Our original objective was the tabulation of Franck-Condon factors and r -centroids for ionization transitions of CO and electronic transitions of CO^+ . Our results for $X(\text{CO}^+) - X(\text{CO})$ and $A(\text{CO}^+) - X(\text{CO}^+)$ showed numerous instances where, within a given v' or v'' progression, the r -centroids did not vary monotonically (tables 1–2). Later we became aware of a number of cases where this nonmonotonic behavior had occurred [9, 7b] for calculations based on both Morse and RKR potentials. Meanwhile, there had appeared a theoretical deduction by Nicholls [10] that $\bar{r}_{v'v''}$ must vary monotonically with respect to wavenumber within a progression.

Nicholls used the Morse function with the Fraser-Jarmain approximation of mean exponential coefficient [11]. His conclusion, however, does not depend on the potential used, but only on the assumption that (10) and (11) are valid. In this case $f(r)$ is the potential function, and (11) leads to the graphical method for determining $\bar{r}_{v'v''}$ [4, 12]

$$G(v') - G(v'') = U'(\bar{r}_{v'v''}) - U''(\bar{r}_{v'v''}) \quad (13)$$

where G is the vibrational term value and U is the potential energy. Since (13) always gives monotonic values within a progression, it may be necessary to revise r -centroids and transition moments determined in this manner.

The transition moment integrals in (7) were evaluated by use of vibrational wave functions based on RKR potentials [13]. These wave functions have been obtained by a method previously discussed by Benesch et al. [14a].

Since the raw wave function is generated as a combination of two unnormalized segments propagated toward each other from either end of the range of interest, an accommodation must be made at the meeting point. The possible methods of arranging for such an accommodation have been discussed elsewhere at length [14]. In the present work, special care

TABLE 1. Transition moment integrals for the $X^2\Sigma^+(\text{CO}^+) - X^1\Sigma^+(\text{CO})$ transition

Entries have been arbitrarily terminated beyond $v''=10$. The last two columns are in Å. The values of $q_{v'v''}$ tabulated here are to be compared with those based on Morse functions [M. Halmann and I. Laulicht, J. Chem. Phys. **43**, 1503–9 (1965)]. The integrals in (7) are obtained by multiplying the ratios of integrals listed and using $(v', v'') = q_{v'v''}^{1/2}$.

v'	v''	$q_{v'v''}$	$(v', r'v'')$ (v', v'')	(v', r^2v'') ($v', r'v''$)	v'	v''	$q_{v'v''}$	$(v', r'v'')$ (v', v'')	(v', r^2v'') ($v', r'v''$)
0	0	0.9644E-00	1.126	1.127	1	6	0.1921E-05	0.666	0.572
1	0	.3566E-01	1.304	1.281	2	6	.7703E-04	0.770	0.735
2	0	.9802E-04	1.839	1.654	3	6	.1414E-02	0.812	0.772
8	0	.7982E-06	1.177	1.176	4	6	.1776E-01	0.884	0.852
0	1	.3383E-01	0.950	0.918	5	6	.1339E-00	0.964	0.929
1	1	.8967E-00	1.135	1.138	6	6	.6424E-00	1.184	1.198
2	1	.6923E-01	1.312	1.290	7	6	.2038E-00	1.356	1.338
3	1	.2435E-03	1.908	1.691	8	6	.6476E-03	2.480	1.926
4	1	.2566E-05	1.078	0.739	9	6	.1555E-03	1.299	1.149
8	1	.1476E-05	1.171	1.170	10	6	.8092E-06	2.343	1.986
10	1	.6424E-06	1.184	1.184	11	6	.1117E-05	1.288	1.236
11	1	.1251E-05	1.186	1.186	12	6	.1308E-05	1.138	1.156
12	1	.5070E-06	1.197	1.197					
0	2	.1586E-02	0.865	0.829	2	7	.7916E-05	0.728	0.689
1	2	.6286E-01	0.954	0.922	3	7	.1560E-03	0.760	0.717
2	2	.8341E-00	1.144	1.149	4	7	.2254E-02	0.813	0.772
3	2	.1006E-00	1.320	1.299	5	7	.2319E-01	0.889	0.860
4	2	.4286E-03	1.958	1.718	6	7	.1412E-00	0.964	0.927
5	2	.6665E-05	1.135	0.830	7	7	.6098E-00	1.195	1.211
6	2	.5311E-06	1.456	1.471	8	7	.2179E-00	1.369	1.350
					9	7	.6308E-03	2.643	1.979
0	3	.8571E-04	0.797	0.754	10	7	.2262E-03	1.350	1.206
1	3	.4451E-02	0.869	0.834	11	7	.1448E-05	2.420	2.008
2	3	.8769E-01	0.958	0.926	13	7	.1127E-05	1.089	1.120
3	3	.7772E-00	1.153	1.160					
4	3	.1301E-00	1.329	1.308	1	8	.5427E-06	1.066	1.101
5	3	.5757E-03	2.042	1.758	2	8	.1620E-04	0.693	0.622
6	3	.2249E-04	1.181	0.958	3	8	.3081E-03	0.781	0.751
7	3	.6232E-06	1.600	1.591	4	8	.3286E-02	0.817	0.777
8	3	.2231E-05	1.166	1.172	5	8	.2738E-01	0.891	0.862
9	3	.5205E-06	1.159	1.161	6	8	.1445E-00	0.962	0.923
11	3	.5928E-06	1.216	1.212	7	8	.5837E-00	1.205	1.225
					8	8	.2392E-00	1.379	1.361
0	4	.5492E-05	0.746	0.699	9	8	.4082E-03	3.138	2.095
1	4	.3297E-03	0.807	0.768	10	8	.5033E-03	1.350	1.242
2	4	.8268E-02	0.874	0.840					
3	4	.1073E-00	0.961	0.928	3	9	.2779E-05	0.741	0.734
4	4	.7262E-00	1.163	1.173	4	9	.3635E-04	0.721	0.675
5	4	.1570E-00	1.337	1.318	5	9	.4595E-03	0.764	0.720
6	4	.7474E-03	2.103	1.788	6	9	.4433E-02	0.817	0.775
7	4	.4340E-04	1.226	1.025	7	9	.3314E-01	0.898	0.872
10	4	.5835E-06	1.146	1.152	8	9	.1505E-00	0.962	0.920
11	4	.9991E-06	1.146	1.147	9	9	.5651E-00	1.218	1.239
					10	9	.2468E-00	1.392	1.374
0	5	.5930E-06	0.785	0.785	11	9	.2017E-03	4.116	2.246
1	5	.2570E-04	0.752	0.707	12	9	.5838E-03	1.420	1.306
2	5	.7541E-03	0.806	0.764	13	9	.1432E-05	0.601	6.320
3	5	.1301E-01	0.880	0.848					
4	5	.1228E-00	0.963	0.930	4	10	.6832E-05	0.770	0.780
5	5	.6811E-00	1.173	1.185	5	10	.6254E-04	0.716	0.666
6	5	.1823E-00	1.346	1.328	6	10	.6689E-03	0.761	0.714
7	5	.7760E-03	2.235	1.842	7	10	.5730E-02	0.818	0.774
8	5	.5198E-04	1.304	1.086	8	10	.3944E-01	0.906	0.884
9	5	.1238E-05	1.870	1.768	9	10	.1463E-00	0.956	0.908
10	5	.5950E-06	1.115	1.153	10	10	.5538E-00	1.229	1.253
11	5	.1120E-05	1.181	1.192	11	10	.2578E-00	1.406	1.388
					13	10	.8231E-03	1.466	1.359

has been taken to insure that the location of the meeting point be such as (a) to prevent either segment from slipping into instability and (b) to provide a relatively large value of the wave function ordinate as a basis for the rescaling of the separate segments prior to joining. Experience has shown that in order to cover all cases of mating, with slopes and ordinates large and small, it is helpful to introduce a monitoring routine for the immediate detection and rectification of pathological cases.

TABLE 2. *Transition moment integrals for the $A^2\Pi_1-X^2\Sigma^+$ transition of CO^+*

The last three columns are in Å. The integrals in (7) are obtained by multiplying the ratios of integrals listed and using $(v', v'') = q_{v'v''}^{1/2}$. The only deletion in this Deslandres array is 0–13 ($q < 0.5 \times 10^{-6}$).

v'	v''	$q_{v'v''}$	$\frac{(v', r^2v'')}{(v', v'')}$	$\frac{(v', r^2v'')}{(v', v'')}$	$\frac{(v', r^2v'')}{(v', v'')}$
0	0	0.4237E-01	1.179	1.179	1.181
1	0	.1131E-00	1.161	1.162	1.163
2	0	.1666E-00	1.145	1.146	1.146
3	0	.1797E-00	1.130	1.130	1.130
4	0	.1585E-00	1.115	1.115	1.115
5	0	.1221E-00	1.101	1.101	1.101
6	0	.8519E-01	1.088	1.087	1.087
7	0	.5496E-01	1.075	1.074	1.073
8	0	.3358E-01	1.063	1.062	1.061
9	0	.1959E-01	1.051	1.050	1.048
10	0	.1114E-01	1.040	1.038	1.036
11	0	.6158E-02	1.029	1.027	1.025
0	1	.1518E-00	1.202	1.203	1.204
1	1	.1926E-00	1.184	1.184	1.184
2	1	.9885E-01	1.167	1.166	1.165
3	1	.1422E-01	1.147	1.143	1.139
4	1	.4447E-02	1.146	1.153	1.161
5	1	.4119E-01	1.125	1.127	1.129
6	1	.7890E-01	1.110	1.111	1.112
7	1	.9512E-01	1.096	1.097	1.097
8	1	.9066E-01	1.084	1.083	1.083
9	1	.7431E-01	1.071	1.071	1.070
10	1	.5541E-01	1.059	1.059	1.058
11	1	.3833E-01	1.048	1.047	1.046
0	2	.2505E-00	1.227	1.228	1.228
1	2	.8117E-01	1.207	1.206	1.204
2	2	.2743E-02	1.205	1.216	1.227
3	2	.7248E-01	1.177	1.178	1.179
4	2	.9599E-01	1.159	1.159	1.159
5	2	.4992E-01	1.143	1.141	1.139
6	2	.6767E-02	1.123	1.116	1.109
7	2	.3288E-02	1.127	1.136	1.146
8	2	.2723E-01	1.107	1.109	1.112
9	2	.5362E-01	1.093	1.094	1.095
10	2	.6855E-01	1.080	1.080	1.081
11	2	.6956E-01	1.068	1.068	1.068
0	3	.2522E-00	1.253	1.253	1.253
1	3	.5236E-03	1.270	1.296	1.318
2	3	.1074E-00	1.217	1.218	1.219
3	3	.7054E-01	1.197	1.196	1.194
4	3	.1025E-02	1.158	1.137	1.113
5	3	.3040E-01	1.170	1.173	1.176
6	3	.7028E-01	1.153	1.153	1.154
7	3	.5856E-01	1.137	1.136	1.135
8	3	.2218E-01	1.121	1.118	1.114
9	3	.1022E-02	1.093	1.074	1.054
10	3	.5758E-02	1.106	1.113	1.120
11	3	.2496E-01	1.090	1.093	1.095
0	4	.1736E-00	1.280	1.280	1.280
1	4	.9207E-01	1.263	1.265	1.266
2	4	.8573E-01	1.240	1.239	1.237
3	4	.3553E-02	1.239	1.250	1.261
4	4	.7630E-01	1.207	1.208	1.209
5	4	.5820E-01	1.188	1.187	1.185
6	4	.4001E-02	1.162	1.151	1.139
7	4	.1388E-01	1.166	1.171	1.176
8	4	.4927E-01	1.147	1.148	1.150
9	4	.5485E-01	1.132	1.131	1.131
10	4	.3186E-01	1.117	1.115	1.113
11	4	.7620E-02	1.101	1.095	1.088
0	5	.8628E-01	1.309	1.308	1.307
1	5	.1917E-00	1.289	1.289	1.290
2	5	.4351E-03	1.218	1.179	1.133
3	5	.9682E-01	1.250	1.251	1.252
4	5	.3713E-01	1.227	1.224	1.221
5	5	.7790E-02	1.224	1.232	1.240
6	5	.6208E-01	1.199	1.200	1.201
7	5	.4859E-01	1.180	1.179	1.177
8	5	.5927E-02	1.157	1.148	1.139
9	5	.6402E-02	1.163	1.171	1.179
10	5	.3430E-01	1.142	1.144	1.146
11	5	.4762E-01	1.128	1.128	1.128
0	6	.3206E-01	1.339	1.337	1.336
1	6	.1766E-00	1.317	1.317	1.316
2	6	.7181E-01	1.299	1.301	1.304
3	6	.6324E-01	1.273	1.271	1.269
4	6	.1862E-01	1.264	1.269	1.274
5	6	.7878E-01	1.238	1.238	1.238
6	6	.1521E-01	1.214	1.209	1.203
7	6	.1157E-01	1.212	1.219	1.225
8	6	.5276E-01	1.191	1.192	1.193
9	6	.4151E-01	1.173	1.171	1.170
10	6	.7227E-02	1.151	1.144	1.135
11	6	.2664E-02	1.163	1.176	1.188
0	7	.9157E-02	1.370	1.368	1.366
1	7	.1001E-00	1.347	1.346	1.346
2	7	.1736E-00	1.325	1.326	1.327
3	7	.8726E-03	1.347	1.347	1.347
4	7	.9872E-01	1.283	1.283	1.284
5	7	.6614E-02	1.250	1.240	1.229
6	7	.4152E-01	1.249	1.252	1.255
7	7	.5698E-01	1.227	1.226	1.225
8	7	.5268E-02	1.200	1.190	1.179
9	7	.1402E-01	1.203	1.209	1.215
10	7	.4586E-01	1.184	1.185	1.186
11	7	.3641E-01	1.166	1.165	1.163
0	8	.2012E-02	1.402	1.400	1.398
1	8	.3885E-01	1.378	1.377	1.375
2	8	.1628E-00	1.355	1.354	1.354
3	8	.9119E-01	1.336	1.338	1.340
4	8	.3093E-01	1.304	1.300	1.296
5	8	.5219E-01	1.294	1.297	1.300
6	8	.5274E-01	1.268	1.266	1.265
7	8	.1508E-02	1.283	1.304	1.323
8	8	.5031E-01	1.238	1.240	1.241
9	8	.3841E-01	1.218	1.215	1.213
10	8	.1301E-02	1.182	1.159	1.133
11	8	.1551E-01	1.196	1.202	1.207
0	9	.3258E-03	1.443	1.439	1.436
1	9	.1104E-01	1.411	1.409	1.407
2	9	.8872E-01	1.387	1.385	1.384
3	9	.1743E-00	1.363	1.364	1.364
4	9	.1598E-01	1.352	1.359	1.365
5	9	.8310E-01	1.316	1.315	1.314
6	9	.4099E-02	1.319	1.333	1.346
7	9	.6895E-01	1.279	1.280	1.280
8	9	.1547E-01	1.252	1.246	1.240
9	9	.1258E-01	1.253	1.260	1.267
10	9	.4873E-01	1.229	1.229	1.230
11	9	.2553E-01	1.209	1.206	1.203
0	10	.3799E-04	1.497	1.489	1.483
1	10	.2314E-02	1.445	1.442	1.440
2	10	.3206E-01	1.421	1.419	1.417
3	10	.1410E-00	1.395	1.394	1.394
4	10	.1289E-00	1.373	1.375	1.376
5	10	.3217E-02	1.317	1.299	1.280
6	10	.8506E-01	1.327	1.328	1.329
7	10	.1063E-01	1.292	1.284	1.275
8	10	.3627E-01	1.291	1.295	1.298
9	10	.4829E-01	1.267	1.265	1.264
10	10	.1165E-02	1.218	1.191	1.160
11	10	.2329E-01	1.241	1.245	1.249
0	11	.2098E-05	1.650	1.609	1.581
1	11	.3642E-03	1.479	1.477	1.475
2	11	.8085E-02	1.457	1.454	1.452
3	11	.6676E-01	1.429	1.428	1.426
4	11	.1717E-00	1.404	1.404	1.404
5	11	.5958E-01	1.385	1.389	1.392
6	11	.4027E-01	1.348	1.344	1.341
7	11	.4330E-01	1.339	1.343	1.346
8	11	.4729E-01	1.310	1.307	1.305
9	11	.3530E-02	1.318	1.333	1.347
10	11	.5099E-01	1.278	1.279	1.280
11	11	.2368E-01	1.255	1.250	1.246
0	12	.9359E-06	1.398	1.421	1.441
1	12	.2899E-04	1.575	1.560	1.548
2	12	.1464E-02	1.494	1.491	1.488
3	12	.2066E-01	1.466	1.463	1.461
4	12	.1093E-00	1.438	1.437	1.436
5	12	.1651E-00	1.413	1.414	1.415
6	12	.1034E-01	1.408	1.418	1.428
7	12	.7871E-01	1.360	1.359	1.358
8	12	.5876E-02	1.364	1.376	1.388
9	12	.6467E-01	1.321	1.321	1.321
10	12	.6190E-02	1.284	1.272	1.260
11	12	.2388E-01	1.291	1.296	1.300
0	13	.1413E-05	1.721	1.675	1.643
1	13	.1713E-03	1.546	1.541	1.536
2	13	.4279E-02	1.506	1.503	1.500
3	13	.4146E-01	1.476	1.474	1.472
4	13	.1489E-00	1.447	1.447	1.446
5	13	.1264E-00	1.424	1.426	1.428
6	13	.1659E-02	1.332	1.300	1.263
7	13	.8401E-01	1.371	1.372	1.373
8	13	.3539E-02	1.318	1.300	1.279
9	13	.4699E-01	1.332	1.335	1.337
10	13	.3228E-01	1.305	1.301	1.298

A number of other checking and diagnostic procedures were instituted in order to seek out computing artifacts and to determine the level of reliability of the results. The effects of changes in integration grid size were examined. Tables were generated for the point-by-point comparison of the function $(d^2\psi/dr^2)/\psi$ with $(U-E)$ as a measure of compliance with the Schrodinger equation, while a macroscopic test consisted of computing self-overlap integrals and overlaps for wave functions of differing vibrational quantum number within the same electronic state. In other words, tables of $\int \psi_{v'} \psi_{v''} dr$ have been computed for all the values of v' and v'' of interest within a single electronic state. The self overlap integrals [squared] were found to be good to 5×10^{-6} and the overlap integrals [squared] of orthogonal functions were no larger than

0.5×10^{-6} . Finally, it was determined that calculated B_v values (i.e., $\text{const. } (v, 1/r^2 v)$) agreed with the corresponding input data values to within 0.0007 to 0.0028 cm^{-1} . Accordingly, we rounded the calculated table entries to four digits, deleting those for transitions having $q_{v'v''} < 0.5 \times 10^{-6}$.

The significant features of tables 1 and 2 are these: (a) For numerous vibrational transitions the ratios of integrals in (10) are not equal. (b) Within a number of v' or v'' progressions the $\bar{r}_{v'v''}$ do not vary monotonically. In other progressions the $\bar{r}_{v'v''}$ are monotonic, but are noticeably not a smooth function of v' (or v''). (c) The onset of nonsmooth behavior correlates with minima in the $q_{v'v''}$, whether or not q is small in an absolute sense. (Fig. 1, table 3.)

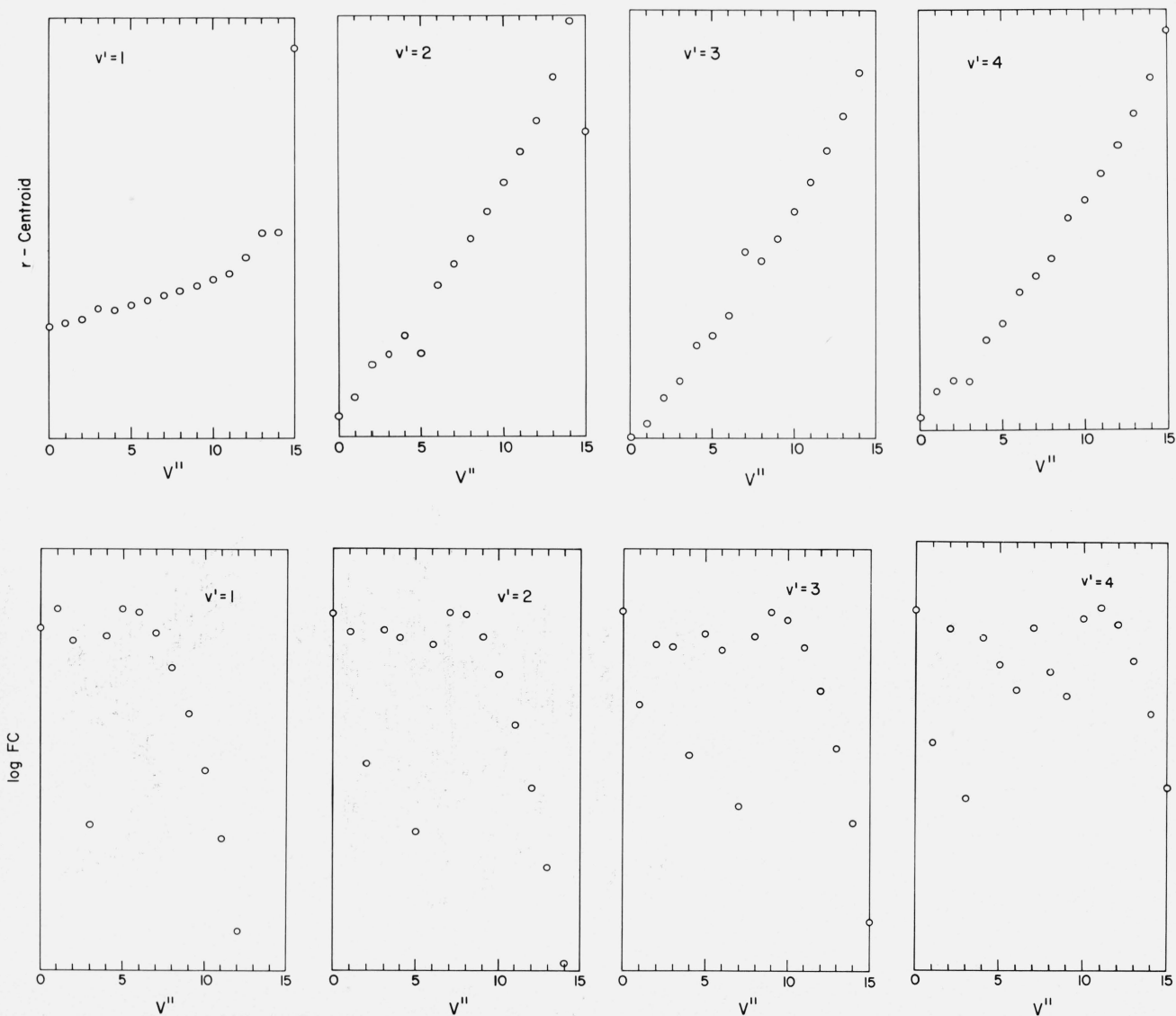


FIGURE 1. $\bar{r}_{v'v''}$ and $\log q_{v'v''}$ for $A^2\Pi_1 - X^2\Sigma^+$, CO^+ , $v' = 1, 2, 3, 4$ progressions. Calculated values for $v'' = 14, 15$ are based on extrapolation of the potential function for the X state and are not considered reliable.

Fraser [4] has stated conditions for the assumed validity of the r -centroid approximation:

- (a) $\mu_A \omega_e \approx 10^4$; μ_A is the reduced mass of the molecule in atomic weight units, ω_e is in cm^{-1} ;
- (b) $0.01 \text{ \AA} < |r_{e'} - r_{e''}| < 0.25 \text{ \AA}$;
- (c) n_{max} is ≈ 10 in (10);
- (d) $q_{v',v''}$ is not small (though small is not specified).

Condition (b) is fulfilled for the CO^+ transition but not for the ionization transition, so that in the latter case, the r -centroid approximation must be assumed to fail under Fraser's criteria. Qualitatively, the non-smooth features are more prominent for the ionization transition.

It has been suggested [15] that the functional form of the electronic transition moment is more important than the choice of wave function in evaluating (4).

However, the choice of wave function (or, more properly, the potential function from which the wave function is generated) can also be significant. RKR-based $q_{v',v''}$ and $\bar{r}_{v',v''}$ are compared in table 4 with previous values based on Morse functions [16]. This comparison does not confirm a statement by Nicholls [17] that the parameters (integrals) are insensitive to the exact potential used. Flinn [18] and Spindler [19] have also shown large differences between RKR and Morse integrals, even for small quantum numbers. From all these results we conclude that wave functions based on RKR potentials should be used where possible so that attention can be centered on the form of the transition moment.

Halevi [20] has assumed, as have others before him, that most of the contribution to the integrals in (7)

	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	<u>.424-1</u>	<u>.152</u>	<u>.251</u>	<u>.252</u>	<u>.174</u>	.863-1	.321-1	.916-2	.201-2	.326-3	.380-4	.210-5	.936-6	.259-6
1	<u>.113</u>	<u>.193</u>	<u>.812-1</u>	.524-3	.921-1	.192	.177	.100	.389-1	.110-1	.231-2	.364-3	.290-4	.141-5
2	<u>.167</u>	<u>.989-1</u>	<u>.274-2</u>	<u>.107</u>	.857-1	.435-3	.718-1	.174	.163	.887-1	.321-1	.809-2	.146-2	.171-3
3	<u>.180</u>	<u>.142-1</u>	<u>.725-1</u>	<u>.705-1</u>	.355-2	.968-1	.632-1	.873-3	.912-1	.174	.141	.668-1	.207-1	.428-2
4	<u>.158</u>	<u>.445-2</u>	<u>.960-1</u>	.102-2	.763-1	.371-1	.186-1	.987-1	.309-1	.160-1	.129	.172	.109	.415-1
5	<u>.122</u>	<u>.412-1</u>	<u>.499-1</u>	<u>.304-1</u>	.582-1	.779-2	.788-1	.661-2	.522-1	.831-1	.322-2	.596-1	.165	.149
6	<u>.852-1</u>	<u>.789-1</u>	.677-2	<u>.703-1</u>	.400-2	.621-1	.152-1	.415-1	.527-1	.410-2	.851-1	.403-1	.103-1	.126
7	<u>.550-1</u>	<u>.951-1</u>	.329-2	<u>.586-1</u>	.139-1	.486-1	.116-1	.570-1	.151-2	.690-1	.106-1	.433-1	.787-1	.166-2
8	<u>.336-1</u>	<u>.907-1</u>	.272-1	.222-1	.493-1	.593-2	.528-1	.527-2	.503-1	.155-1	.363-1	.473-1	.588-2	.840-1
9	.196-1	<u>.743-1</u>	.536-1	.102-2	.548-1	.640-2	.415-1	.140-1	.384-1	.126-1	.483-1	.353-2	.647-1	.354-2
10	.111-1	<u>.554-1</u>	<u>.685-1</u>	.576-2	.319-1	.343-1	.723-2	.459-1	.130-2	.487-1	.116-2	.510-1	.619-2	.470-1
11	.616-2	.383-1	<u>.696-1</u>	.250-1	.762-2	.476-1	.266-2	.364-1	.155-1	.255-1	.233-1	.237-1	.239-1	.323-1

TABLE 3. Franck-Condon factors for the $A^2\Pi_1 - X^2\Sigma^+$ system of CO^+

Nonmonotonic r -centroids were found, generally, where the q 's of neighboring bands in a progression differed by a factor of some 10^2 . The transition with the smaller q , then, may have an r -centroid which breaks the monotonic series, while the band itself, falling in a hole between Condon loci, will be extremely weak or unobserved. Bands which have been observed are underlined. For a compendium of experimental data see P. H. Krupenie, "The Band Spectrum of Carbon Monoxide," National Standard Reference Data Series, National Bureau of Standards NSRDS-NBS No. 5 (1966).

TABLE 4. $q_{v'v''}$ and $\bar{r}_{v'v''}$ for the $A^2\Pi_1-X^2\Sigma^+$, CO^+ system

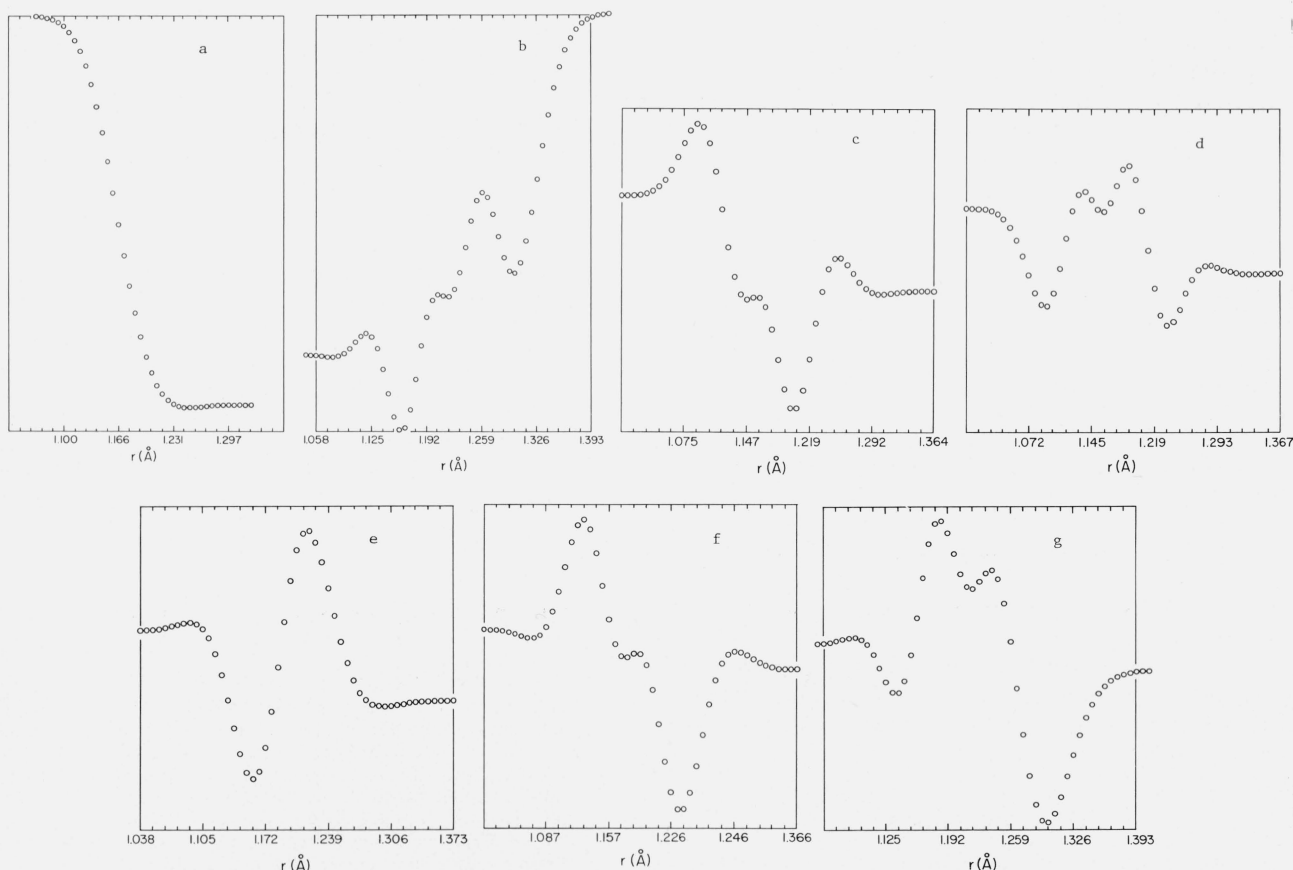
Each entry for $q_{v'v''}$ includes the power of 10 (e.g., $-3=10^{-3}$) by which it is multiplied. Most differences between RKR and Morse data taken from ref. 16 are small. Only the values showing large differences are compared.

$v' - v''$	$q_{v'v''}$		$\bar{r}_{v'v''}$ (Å)	
	RKR	Morse	RKR	Morse
4-1	4.447-3	5.796-3	1.146	1.136
2-2	2.743-3	3.228-3	1.205	1.191
6-2	6.767-3	4.973-3	1.123	1.130
7-2	3.288-3	5.155-3	1.127	1.116
1-3	5.236-4	5.677-4	1.270	1.234
4-3	1.025-3	5.787-4	1.158	1.182
5-3	3.040-2	3.336-2	1.170	1.166
9-3	1.022-3	2.345-4	1.093	1.110
10-3	5.758-3	8.830-3	1.106	1.098
3-4	3.553-3	4.186-3	1.239	1.223
6-4	4.001-3	2.730-3	1.162	1.174
2-5	4.351-4	3.505-4	1.218	1.268
9-5	6.402-3	9.005-3	1.163	1.153
10-6	7.227-3	4.869-3	1.151	1.161
3-7	8.726-3	1.054-3	1.347	1.303
8-7	5.268-3	3.702-3	1.200	1.212
7-8	1.508-3	2.289-3	1.283	1.253
10-8	1.301-3	4.986-4	1.182	1.205
5-10	3.217-3	2.976-3	1.317	1.347
10-10	1.165-3	5.736-4	1.218	1.252
1-12	2.899-5	4.088-5	1.575	1.539
7-13	1.659-3	3.046-3	1.332	1.393

comes from a narrow region around $\bar{r}_{v'v''}$. This need not be so. $\int \psi_{v'} \psi_{v''} r dr$ is evaluated numerically as

$\sum_r \psi_{v'} \psi_{v''} r \Delta r$. Plots of such cumulative sums as a function of r (fig. 2) may show regions having large slope which indicate large contribution to the integral in that r interval. Three general effects occur. Figure 2(a) describes an integral where there is no contribution except very near the average value of r . If the wave functions were delta functions then such sums would be step functions, and only at a single value of r would there be a contribution to the integral. In such instances the ratios of integrals in (10) would be equal. For functions whose product $\psi_{v'} \psi_{v''}$ is sharply peaked, whether for small or large overlap integral, a plot closely similar to figure 2(a) would be expected. Figure 2(b) shows smaller oscillations with the most significant contribution to the integral coming at large r . Figure 2(c)-(g) shows several regions with significant slope; the sums show large oscillations about the final value of (v', rv'') .

Figure 2(c)-(g) describes what is likely true of many integrals, even for q as large as 0.1 (no integral for larger q has been checked, except 0-0, X-X). In

FIGURE 2. $\sum \psi_{v'} \psi_{v''} r \Delta r$ for $A-X$, CO^+ transitions.

(a) 1-0, (b) 2-6, (c) 6-2, (d) 7-2, (e) 2-2, (f) 4-3, (g) 2-5. The ordinate is 0 for smallest r ; the ordinate is (v', rv'') for largest r . $q_{v'v''}$ decreases from (a) = 0.1 to (g) = 0.0004.

table 2 and the ratios (10) are not closely the same for $q \leq 2 \times 10^{-2}$. In table 1 the results are erratic. Only a detailed examination of all integrals would reveal whether the wave functions show delta-function like behavior as in figure 2(a).

Nicholls and Jarmain [12] state: "Comparison between the calculated values of $\bar{r}_{v'v''}$ of a band system and the ranges of r between the classical turning points for each of the levels v' and v'' has shown that $\bar{r}_{v'v''}$ lies within, or close to the region which is common to both ranges." This is generally true, but James [21] has already pointed out examples where $\bar{r}_{v'v''}$ lie outside the range of turning points and do not represent a meaningful average r . Since products of the wave functions do not become insignificantly small till 0.06 Å beyond the turning points, it is not surprising if an r -centroid lies beyond the turning points, providing tails of both wave functions are involved. Table 5 shows some of the extreme examples we have obtained. The A-X, 0-0 and 1-0 transitions illustrate the influence of wave function tails. For 0-0 the turning points do not overlap by 0.026 Å; for 1-0 they overlap slightly. In both instances, $\bar{r}_{v'v''} \approx \frac{r''_{\max} + r'_{\min}}{2}$.

Since the ground states of CO and CO⁺ have nearly the same r_e and nearly the same potential shapes, almost all the ionization transition probability gets dumped into a single transition for low v . The 0-0 transition has $q = 0.964$. Large values of q are found for other members of the $\Delta v = 0$ sequence, where, for example, the 7-7 entry is still above 0.6.

TABLE 5. $\bar{r}_{v'v''}$ lying outside turning points for some A-X, CO⁺ transitions

Turning points are taken from ref. 13. $\bar{r}_{v'v''}$ and turning points are in Å. Each entry for $q_{v'v''}$ includes the power of 10 (e.g., $-3 = 10^{-3}$) by which it is multiplied.

$v' - v''$	$\bar{r}_{v'v''}$	A ² Π ₁		X ² Σ ⁺		$q_{v'v''}$
		r_{\min}	r_{\max}	r_{\min}	r_{\max}	
0-0	1.178	1.191	1.304	1.071	1.165	4.237-2
11-0	1.029	1.046	1.634	1.071	1.165	6.158-3
0-6	1.339	1.191	1.304	0.977	1.330	3.206-2
0-7	1.370			0.968	1.350	9.157-3
0-8	1.402			0.961	1.370	2.012-3
0-9	1.443			0.954	1.390	3.258-4

Halevi [20] has expanded the transition moment in a Taylor series centered about the r -centroid and has obtained a correction term to $R_e^2(\bar{r}_{v'v''})q_{v'v''}$ which depends on the second derivative of $R_e(\bar{r}_{v'v''})$. This correction term may have little quantitative significance when (10) is not valid.

3. Conclusions

We have drawn several conclusions regarding the determination of electronic-vibrational transition probabilities from a study of two electronic transitions:

(1) The r -centroid approximation for obtaining electronic transition moments and band strengths

may prove to be not continuously valid along the significant portion of a vibrational progression. The band strength may not always be factored as $R_e^2(\bar{r}_{v'v''})q_{v'v''}$ for nonlinear R_e .

(2) Interpretation of the r -centroid as an average r is not always meaningful.

(3) The transition moment integrals are sensitive to the potential used; they should be calculated from RKR potentials where possible.

(4) The Fraser criteria are not sufficient to insure the validity of the r -centroid approximation.

(5) The series expansion for the transition moment may be used when the r -centroid approximation fails.

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